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SELECTION OF A REAGENT TO SEPARATE LEAD AND SELENIUM CONTAINED IN THE SLIME OF THE SULFURIC ACID WORKSHOP OF BALKHASH COPPER PLANT

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ABSTRACT

Balkhash Copper Plant obtains sulfuric acid from metallurgical gases, which is received from melted copper charge and converted matte. Slime from wet gas scrubbing is discharged into the dump. It results in the loss of more than 30% of selenium from the copper anode slimes received at this plant. This work presents the compositions of lead and selenium and the material composition of these elements in slime samples taken in different years. We presented the results of a study on the conversion of lead and selenium into different phases using the direct hydrometallurgy method. Perchloric acid, ammonium perchlorate and EDTA-2Na were used as leaching reagents. The analyis was performed through the atomic emission method, X-ray fluorescence, X-ray phase and infrared spectroscopy on new generation devices. We revealed Pb, Se, Re, Al, Si, S, Ca, Fe, Cu, Zn, Sr, Cd, I, Hg, Ni, Br, Bi, As in the samples with the composition that varies over a wide range. This article presents only the content of selenium and lead and their quantitative material compositions. The main element in all samples of slime is lead (50-60 mass %) and the substance is lead sulfate. The content of selenium is different (15.5 - 0.58 mass %), as well as the material composition. We found 13 selenium-containing substances: elemental selenium of various modifications, lead and mercury salts of various selenium acids. Lead is almost completely removed from the slime in the solution only with EDTA-2Na solution and selenium is concentrated in the sediment.

***KEYWORDS:** Slime of the sulfuric acid workshop of the Balkhash Copper Plant, Lead, Selenium, Leaching, Perchloric acid, ammonium perchlorate, EDTA-2Na & Material Composition*

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Original Article

1. INTRODUCTION

When processing the copper charge into the target metal, two copper plants of Corporation "Kazakhmys" obtain four selenium-containing man-made mineral formations: wash sulfuric acid, slime from the sulfuric acid and electrolyte workshops, dry electrical filter dust. To date, from these formations, as in the world, selenium is extracted only from Copper Anode Slimes (CAS) of both plants. Dust is sent abroad, the slime of Sulfuric Acid Workshops (SAW) is dumped. A specific feature of the SAW technology of the Balkhash Copper Plant (BCP), as compared to other non-ferrous metallurgy plants in Kazakhstan, is the discharge of pulp from scrubbing metallurgical gases without first settling slime into the dump and high selenium content in the slime (4.6 - 37 mass %) [1]. It results in the loss of ≥ 30% of the metal obtained from CAS.

In world practice, 90% of selenium is obtained from CAS and only 10% from slime from the production of sulfuric acid in chemical plants and sulfuric acid in pulp and paper industries [2, 3]. The SAW slime from non-ferrous metallurgy plants, containing mainly lead and, in small quantities, rare and some non-ferrous metals, is mainly dumped and only partially stored or partially processed at lead plants.

Analysis predicts a deficiency of selenium due to an increase in its consumption by various industries, in particular for the production of solar cells, and a reduction in the CAS volume due to the introduction of roasting-leaching-electro extraction technology for copper chalcopyrite ores [2, 3]. Involvement in the sphere of production of technogenic selenium-containing formations of the SAWs of the metallurgical industry with a high content of selenium will stabilize its production. However, technologies for producing selenium from them are currently lacking.

Analysis of the available periodical and educational classical literature showed that, despite the presence of existing technologies for obtaining selenium from CAS, research in this direction is intensive [4-6]. The works on the development of technologies for its extraction from the slime of the SAWs of non-ferrous metallurgy are single [7-11]. They are mainly held in Russia. Transfer of technologies for obtaining selenium from CAS and slime from the chemical and pulp and paper industry to slime from SAWs of non-ferrous metallurgy plants, in particular to slime from BCP SAWs, is not possible.

Involvement in the SAW slime production area at BCP is reasonable, considering the high content of selenium in it; the separation of slime into an independent technogenic formation when introducing the technology for extracting rhenium from washing sulfuric acid (a solution from pulp filtration) and the ability to bring selenium extracted from slime to standard condition, using the existing technology for production from CAS at BCP [12].

In the SAW slime (hereinafter: slime) of some copper and nickel plants, the selenium content ranges from 0.18 to 46 mass %, and the lead content ranges from 0.17 to 65 mass % (Table 1) [9, 10].

Table 1: Content of Selenium and Lead in the Slime of Sulfuric Acid Workshops of Copper Plants in Kazakhstan and some Nickel Plants in Russia

Country	Enterprise	Content, Mass %	
		Se	Pb
Kazakhstan	Balkhash Copper Plant	4.60 - 12.5	46.2 -57.9
	Zhezkazgan Copper Plant	0.18 - 0.3	56.5 - 65.0
Russia	Kolskaya MMC OJSC:		
	Severonikel ("gas scrubbing cakes")*	46.0	0.17
	Pecheneganikel ("gas scrubbing cakes")*	12.5	25.60

Note: * **-** production Terminology

In the slime from BCP SAWs, in comparison with the “cakes” of Severonikel, the lead content is, on an average, 309 times more, selenium content is 5.4 times less, and that from Pecheneganikel is 2 and 1.5 times less, respectively. The selenium content in the slime from BCP is 5-12 times less than that of lead. Extracting lead from the slime into the solution will allow concentrating selenium in the sediment.

The authors of [9, 10] performed studies on leaching of “cakes” with water, solutions of sulfuric acid and sodium chloride to obtain precipitates enriched in selenium. It is shown that the key factors of increased composition of the selenium content in the sediment are the chemical composition of the slime and the nature of the leaching reagent. We have shown in the work [13] that the use of a sodium chloride solution as a leaching reagent in relation to BCP slimes

made it possible to selectively extract lead into the solution and concentrate selenium in the sediment. However, the use of this reagent industrially is not economically feasible. Hence, the high rates of lead extraction into the solution were obtained by multiple sequential leaching of one sample of slime at high S:L ratios and temperature.

Intensive work on obtaining lead from various technogenic formations of non-ferrous metallurgy is carried out by scientists of Russia, which is experiencing a shortage in this metal. In order to extract lead into the solution, they studied inorganic and organic substances [14–20]. However, there is no information on selenium in these publications.

To transfer lead and selenium into different phases, we studied perchloric acid, ammonium perchlorate, and EDTA-2Na. The choice of reagents is based on the solubility of lead salts formed during the interaction of lead sulfate with these substances, as well as on the ability of ammonium salts to interact with lead sulfate [21].

The interaction of lead sulfate with solutions of these substances proceeds according to the following reactions:

$$PbSO_4 + 2HClO_4 = Pb(ClO_4)_2 + H_2SO_4, \quad (1)$$

$$PbSO_4 + 2NH_4ClO_4 = Pb(ClO_4)_2 + (NH_4)_2SO_4, \quad (2)$$

$$PbSO_4 + C_{10}H_{14}O_8N_2Na_2 = C_{10}H_{12}O_8N_2Na_2Pb + H_2SO_4 \quad (3)$$

where $C_{10}H_{14}O_8N_2Na_2$ – (EDTA-2Na).

2. EXPERIMENTAL PART

2.1 Materials, Reagents

Slimes from BCP SAWs were sampled in 2011, 2014 and 2018. Perchloricacid, ammonium perchlorate, and EDTA-2Na were used as pure chemical reagent**.** Solutions were prepared taking the solubility of the starting materials and the resulting lead salts into account.

2.2 Analysis Methods

X-Ray Fluorescence - XRF (Venus 200 spectrometer with wave dispersion, PANalytical B.V.), chemical (atomic emission Optima 2000 DV spectroscope (USA, PerkinElmer), X-ray Phase - XPA (D8 Advance (BRUKER) diffractometer, infrared spectroscopy - IR spectroscopy (IR - Thermo Nicolet Avatar 370 FTIR Spectrometer). The identification of lead and selenium compounds and their groups was carried out according to [22 - 30].

2.3. Experiment Technique

The experiments were carried out on an installation including a thermostat, a cell with a jacket and a reflux condenser, a stirrer with an adjustable speed (Figure 1). A solution of the corresponding reagent was poured into the cell, heated to a pre-determined temperature; a slime sample was poured portion wise with the stirrer on. After a predetermined time, the pulp was filtered under vacuum; the cake on the filter was washed with distilled water from the initial solution and dried at 105°C to constant weight.



1: Thermostatically-controlled Cell with a Jacket, 2: Stirrer with an adjustable Speed, 3: Thermostat
Figure 3:Leaching Installation

Slimes were analyzed for all elements; cakes and solutions were analyzed only for lead and selenium; slimes and cakes were analyzed for the material composition.

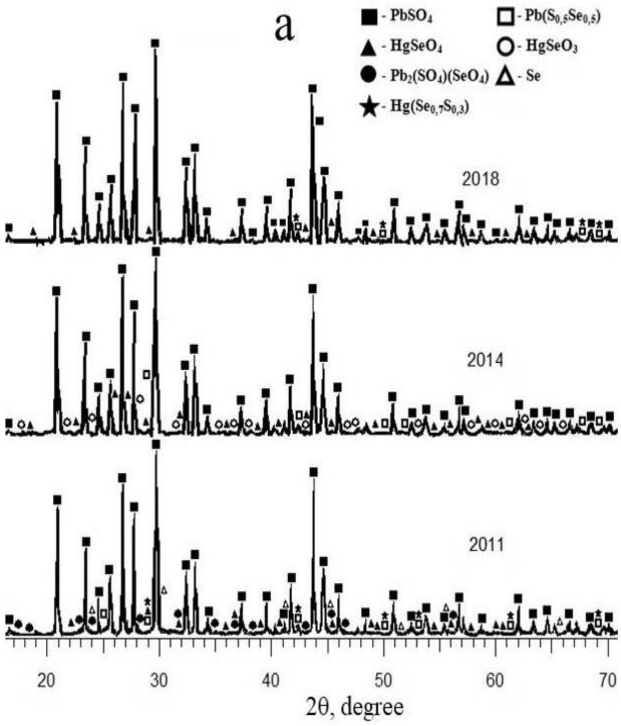
3. RESULTS AND DISCUSSIONS

3.1. Chemical and material slime compositions

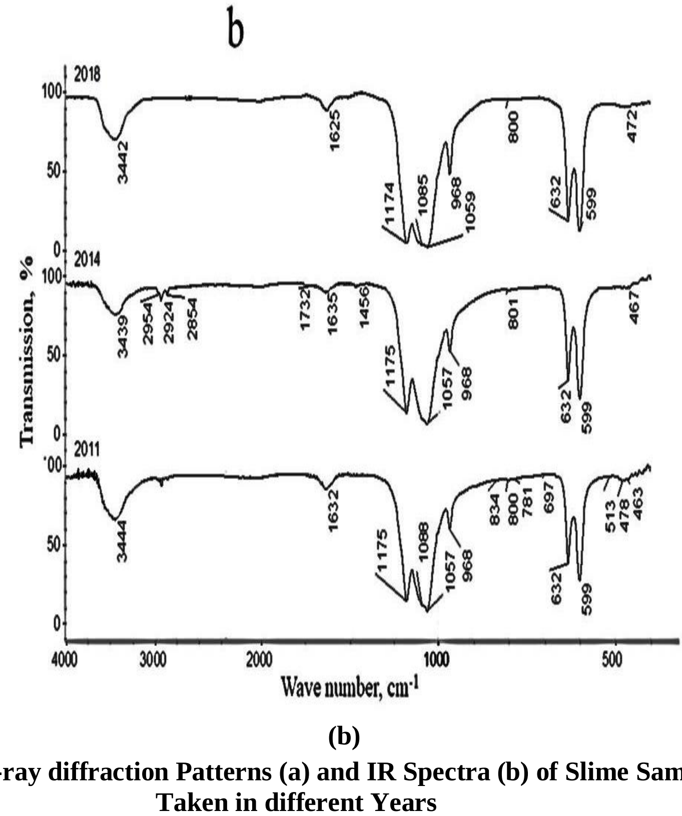
Slime samples were washed with water from acid, dried at 105°C to constant weight, triturated, averaged by quartering. After drying, they changed the white-pink color to black. The color change is caused by the transformation of elemental selenium of the red modification into black when drying samples of slime at 105 °C. In each sample of slime, 18 elements were found: Pb, Se, Re, Al, Si, S, Ca, Fe, Cu, Zn, Sr, Cd, I, Hg, Ni, Br, Bi, and as, the content of which varies over a wide range. Table 2 shows only the contents of lead and selenium and their quantitative and material compositions according to the diffraction patterns (Figure 2a), and the IR spectra are also shown in the same figure.

Table 2: Content of Lead and Selenium and their Material Composition in samples of Slime Taken in different Years

Material Composition (XRF) Content,%												
$PbSO_4$	$PbSO_4PbSeO_4$	$PbSeO_3$	$PbS_{0.5}Se_{0.5}$	Se	Se	SeO_2	$HgSeO_4HgO$	$HgSeO_4$	$HgS_{0.7}Se_{0.3}$	$PbSO_42PbO$	$Cu_{1.8}Se$	Hg_2SeO_3
2011 slime (content, mass %: 51.2 Pb, 12.5 Se)												
75.2	4.8	1.0	0.4	3.9	0.3	3.4	1.0	5.9	0.2			
2014 slime (content, mass %: 57.9 Pb, 4.6 Se)												
90.5			1.5					1.4		4.2	1.5	0.8
2018 slime (content, mass %: 60.7 Pb, 0.58 Se)												
96.4			1.5					1.4	0.3			



(a)



(b)

Figure 2: X-ray diffraction Patterns (a) and IR Spectra (b) of Slime Samples Taken in different Years

Table 2 shows that $PbSO_4$ is the main substance of the slime, with the content in the samples, %: 75.2 (2011), 90.5 (2014), and 96.4 (2018). However, the samples differ significantly by the content of selenium and its material composition. In that way, in 2011 slime, 9 different substances were found (Se content: 12.5 mass %); in 2014 slime,

respectively - 5 (Se content: 4.6 mass %); in 2018 sludge - 3 (Se content: 0.58 mass %). Elemental selenium was found in slimes of 2014 and 2018; some substances were not found in comparison with 2011 slime. It is probably due to the deposition of diffraction reflections of selenium-containing substances of low intensity with diffraction reflections of $PbSO_4$ of strong intensity and due to different selenium composition. A total of 13 different substances of selenium were found in the slime, but their content is very insignificant (4.8 - 0.2%). For these reasons, the presence of certain selenium-containing substances (<1%) is in question.

The IR method confirmed the presence of $PbSO_4$ (1175 (1174), 1057 (1059), 968, 632, 599 cm^{-1}) [23 - 26], $PbSeO_4$, (834, 800 (801) cm^{-1}) [24] in all samples of slime, and, perhaps, SeO_3^{2-} (800 (801) cm^{-1})[27], and the organic component in the 2014 sample [28, 29], which, meanwhile, negatively affected all types of instrumental methods used to analyze precipitation from experiments [31]. The presence of organic compounds is due to the introduction of another deposit into the charge of coal this year.

1.4. Leaching with Perchloric Acid Solutions, Ammonium Perchlorate, EDTA-2Na

Experimental conditions: sample - 50 g. S:L = 1:10, time - 1 h, temperature - 25 °C. The results are presented in Table 3 which shows that lead is well extracted into the solution from all slime samples only with an EDTA-2Na solution.

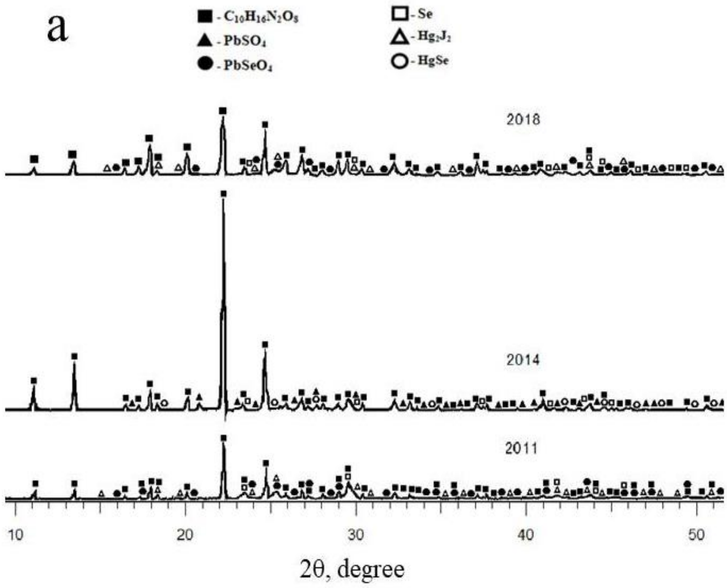
Table 3: The effect of the nature of the reagent on the behavior of lead and selenium during leaching of slime from different years (content in slime, mass %: 51.2 Pb, 12.5 Se (2011); 57.9 Pb, 4.6 Se (2014); 51.2 Pb, 12.5 Se (2018)

Slime, Year	Cake					Filtrate			
	Yield, %	Content, Mass %		Extraction, %		Concentration, mg/dm^3		Extraction, %	
		Pb	Se	Pb	Se	Pb	Se	Pb	Se
Perchloric acid (concentration – 120 g/dm^3)									
2011	92.80	55.14	13.30	99.94	99.20	233	0.24	0.46	0.002
2014	97.12	59.49	4.68	99.80	98.81	243	0.33	0.42	0.007
2018	93.72	64.58	0.62	99.72	100.0	228	0.52	0.37	0.360
Ammonium perchlorate (concentration – 80 g/dm^3)									
2011	95.20	53.60	13.02	99.99	99.16	70	0.40	0.14	0.003
2014	95.90	60.10	4.79	99.54	99.86	70	0.50	0.12	0.011
2018	95.68	63.17	0.61	99.08	100.62	70	0.56	0.11	0.010
EDTA-2Na (concentration. – 100 g/dm^3)									
2011	70.00	0.37	18.03	0.49	100.97	50700	0.27	99.02	0.004
2014	77.56	0.40	5.90	0.53	99.50	57300	not detected	99.00	0.000
2018	68.30	0.40	0.84	0.47	98.92	60000	not detected	98.84	0.000

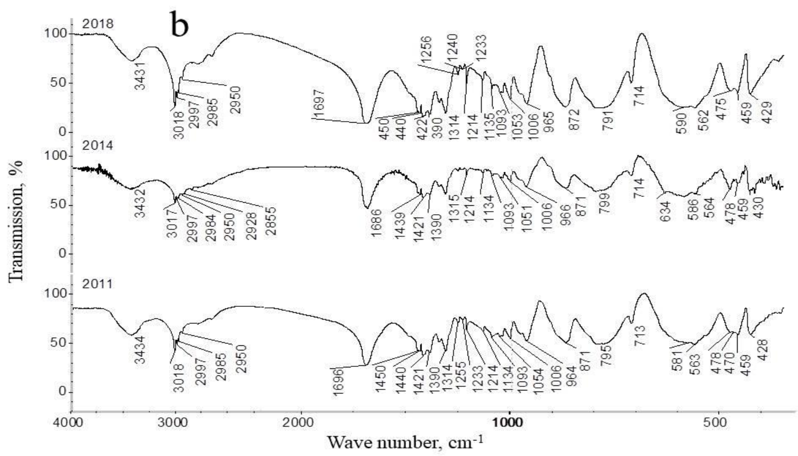
As evidenced by its extraction into the solution (~ 99.0%), the concentration in solutions (50 - 60 g/dm^3), and the content in cakes (0.37 - 0.40 mass %). However, the yield of cakes is high (68.3 - 77.56%) due to EDTA ($C_{10}H_{16}N_2O_8$), which was detected by XPA and IR spectroscopy (Table 4, Figure 3). Acid is the main substance in all cakes: 68.8 – 84.6 %. The introduction of sodium hydroxide into the EDTA-2Na solution during leaching of the slime prevented the precipitation of acid. For instance, when 2011 slime was leached, cake yield was 18.74% of the weight taken, the lead content and the selenium content increased to 0.8 mass% and 65.54 mass %, respectively (Table 4, Figures 3, 4).

Table 4: Chemical and Material Compositions of Cakes from Leaching of Slime with EDTA-2Na solution (information on cakes from Leaching of Slime with solutions of perchloric acid and Ammonium Perchlorate is not given because of the Identity with the crude slime)

Material Composition (XRF)						
content,%						
$PbSO_4$	$C_{10}H_{16}N_2O_8$	Se	Se	HgSe	$Cu_{1.8}Se$	$PbSeO_4$
Cake from 2011 slime leached with EDTA-2Na (content, mass %: 0.37 Pb, 18.03 Se)						
	68,8	12.5	10.6	2.4		
Cake from 2011 slime leached with a EDTA-2Na solution **and** sodium hydroxide (content, mass %: 0.84 Pb, 65.54 Se)						
10		51.6	4.4	16.9		
Cake from 2014 slime leached with EDTA-2Na (content, mass %: 0.4 Pb, 5.9 Se)						
6.9	75.6	1.1		2.0	1.9	
Cake from 2018 slime leached with EDTA-2Na (content, mass,%: 0.4 Pb, 0.84 Se)						
	84.6	1.9				11.6



(a)



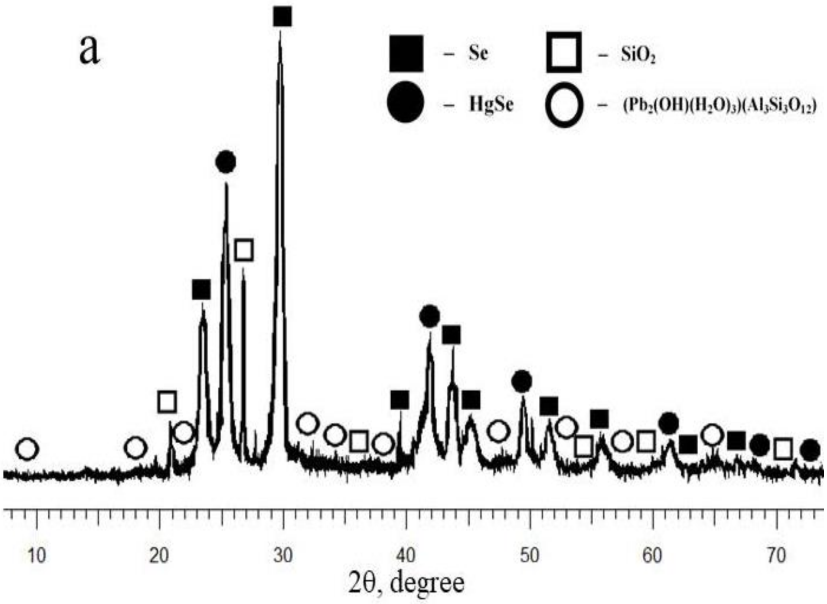
(b)

Figure 3: Diffraction Patterns (a) and IR Spectra (b) of Cakes from Slime of different Years Leached with EDTA-2Na

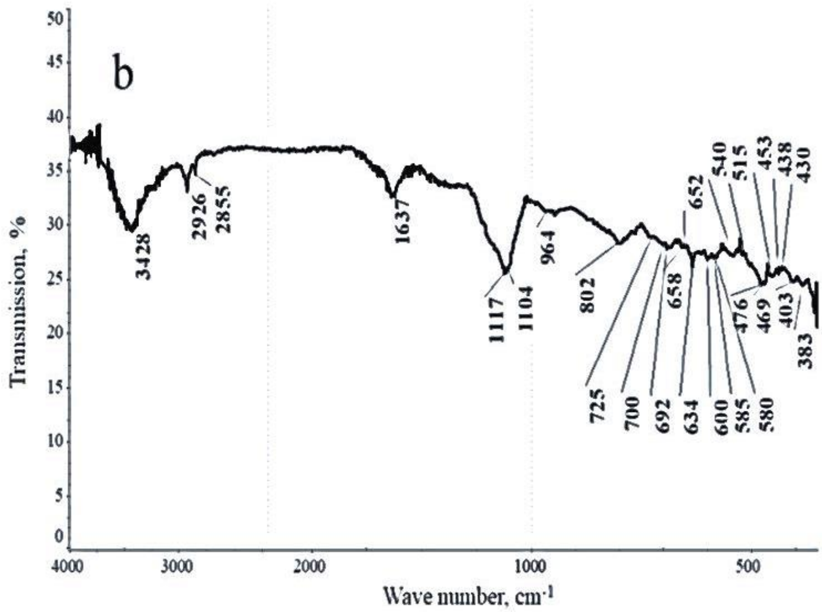
EDTA is formed due to the interaction of sulfuric acid released by reaction (3) and interacting with EDTA-2Naby reaction with precipitation:

$$H_2SO_4 + C_{10}H_{14}O_8N_2Na_2 = C_{10}H_{16}N_2O_8\downarrow + Na_2SO_4 \quad (4)$$

When leaching all the samples of the slime, selenium remains almost completely in cakes (its maximum concentration in the filters is 0.56 mg/dm^3) (Table 3) with a 1.4-fold increase in content compared to the crude slime, and with 5.2-fold increase after washing the cake with sodium hydroxide solution (2011 slime) (Tables 3, 4).



(a)



(b)

Figure 4: Diffraction Patterns (a) and IR Spectra (b) of Cake after Removal of EDTA

The material composition of cakes detected by XRF and IR spectrometry methods is different (Table 4, Figure 3), which is explained by the structural properties of substances and the sensitivity of methods and devices. In that way, XRF identified a different amount of selenium-containing substances in all cakes: Se of two modifications, HgSe (2011); Se, HgSe, $Cu_{1.8}Se$ (2014); Se, $PbSeO_4$ (2018). IR spectroscopy did not give positive results for the following reasons. Firstly, this method determines the group composition of substances formed due to covalent bonds, therefore, as compared to XRD, Se and substances formed due to ionic bonds were not detected. For example, HgSe. Secondly, the absorption bands of EDTA overlapped the absorption bands of selenium and lead-containing groups at different ratios of compounds in the sediments. This is confirmed by eliminating the possible precipitation of acid. In cake, selenium is present in the form of 2 substances: Se of two modifications (60% in total), HgSe (16.9 mass %).

Therefore, based on the comparative results of the two methods and properties of chemical selenium-containing substances, we can conclude that the cakes contain elemental Se of various modifications, $PbSeO_3$, SeO_3^{2-}, HgSe, and $PbSeO_4$. Obviously, these are the substances that are mainly contained in the slime.

Our assumptions about the effective use of perchloric acid and a solution of ammonium perchlorate were not confirmed, despite the high solubility of $Pb(ClO_4)_2{\cdot}3H_2O$ (~ 500 g/dm^3, 25 ^{0}C). This is evidenced by the low concentration of lead in solutions (~ 0.233 and ~ 0.07 g/dm^3, respectively), the degree of extraction into the solution (~ 0.4 and ~ 0.11%) and the high content in cakes (53.4 and 63.58 mass %). Lead sulfate in cakes was detected by both methods. The Gibbs energy values calculated using the data of [32] for both reagents indicate the probability of the occurrence of only the direct exchange reaction (1) (ΔG_{298} = -21.347 kJ/mol). Perchloric acid, as strong ($K_a=10^{10}$), displaces weaker sulfuric acid ($K_a=10^3$) from lead sulfate, the resulting $Pb(ClO_4)_2$ and H_2SO_4, supposedly contained in the solution, should interact with each other with the formation of $PbSO_4$ and, possibly, a slightly soluble salt $Pb(HSO_4)_2$. It is likely that the forward and reverse reactions (1) proceed at different rates. Thermodynamically, lead sulfate does not interact with ammonium perchlorate, despite the fact that there is information in the literature on the dissolution of PbSO4 i in solutions of ammonium salts [21].

CONCLUSIONS

Selenium is obtained from copper anode slimes at Balkhash Copper Plant. However, there is also an alternative raw material enabling to increase its yield by more than 30%, - slime from the sulfuric acid workshop. The selenium content in the slime (12.5 - 0.58 mass %) depends on the composition of the raw materials processed. It is established that lead sulfate is the main substance in the slime. Selenium is found not only in the form of a simple substance as known from the publications, but also in the form of various salts of lead and mercury, and various acids of selenium. The selenium content increases significantly when the slime is leached out with an EDTA-2Na solution due to the almost complete extraction of lead in the solution and selenium concentration in the precipitate in the form of elemental, mercury selenide and lead selenate.

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